



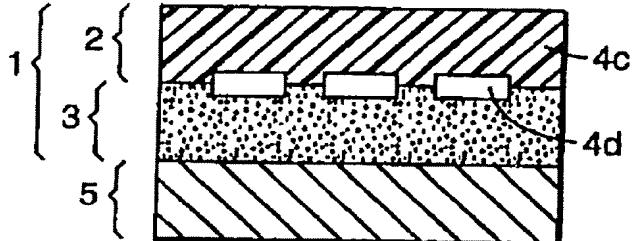
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## (54) Title: TAMPER INDICATING MULTILAYER SHEET

## (57) Abstract

The present invention refers to a multilayer sheet (1) comprising a flexible backing (2) and a pressure-sensitive adhesive layer (3) for attaching the multilayer sheet to a smooth and rigid surface (5), wherein the pressure-sensitive adhesive is completely removable from the surface (5) and is selected to exhibit for an adhesive layer with a thickness of 300  $\mu$ m a 90° peel adhesion of between 20 and 85 N/inch from glass after a dwell time of 3 days at a temperature of 70 °C. The flexible backing (2) preferably comprises at least one damagable layer (4) and shows intralayer failure when peeling off the multilayer sheet (1) from the surface (5). The present invention furthermore refers to a pressure-sensitive adhesive which is obtainable by polymerizing a precursor comprising a) a monomer component which contains one or more alkyl acrylates, the alkyl groups of which have an average of 4-14 C atoms, and 2-8 phr of at least one copolymerizable monomer having a polar group, b) 5-15 phr of hydrophobic silica, c) one or more polymerization initiators, and d) one or more cross-linker compounds in a concentration resulting in a cross-link density obtainable by using hexanedioldiacrylate as a reference cross-linker compound in a concentration between 0.06 and 0.14 phr. The present invention furthermore refers to a pressure-sensitive adhesive which is obtainable by polymerizing a precursor comprising a) a monomer component which contains one or more alkyl acrylates, the alkyl groups of which have an average of 4-14 C atoms, and 8-20 phr of at least one copolymerizable monomer having a polar group, b) 5-15 phr of hydrophobic silica, c) one or more polymerization initiators, and d) one or more cross-linker compounds in a concentration resulting in a cross-link density obtainable by using hexanedioldiacrylate as a reference cross-linker compound in a concentration between 0.06 and 0.11 phr.



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## TAMPER INDICATING MULTILAYER SHEET

Field of the Invention

5        The invention relates to pressure-sensitive adhesive coated multilayer sheet useful as removable stickers for application to smooth and rigid surfaces such as glass or painted metal surfaces whereby the stickers preferably exhibit tamper-proof characteristics. The invention furthermore relates to pressure-sensitive adhesive materials which are useful in these multilayer sheets.

10      Background of the Invention

Multilayer sheets useful for tamper-proof labels and stickers are known. WO 95/29474 describes, for example, a sticker for attachment to the inside of a vehicle window. DE 44 05 945 also describes a tamper-proof sticker for application to a transparent surface such as a windshield. DE 43 14 579 describes a tamper-proof windshield sticker containing a hologram. Tamper-proof stickers known in the art are designed, to have very high adhesion to smooth surfaces such as glass and to give permanent bonding, and they can be removed only with the aid of solvents and/or mechanical scraping.

20      In some cases, transparent polymeric foils or sheets such as, for example, polyurethane foils are laminated onto the inner surface of windshields. Having to use solvents and/or mechanical tools for temporary stickers is inconvenient, and polymeric sheets or foils can easily be damaged by solvents and scraping. Thus there is a need for providing a multilayer sheet useful, for example, as a sticker, which is readily removable from smooth and rigid surface and preferably furthermore exhibits tamper-proof characteristics.

25      Multilayer sheets which are useful for the preparation of a sticker which has high enough adhesion to render it tamper-proof, yet at the same removable without the aid of solvents or mechanical scraping are not available in the prior art.

30      Brief Description of the Drawings

The present invention refers to a multilayer sheet (1) comprising a flexible backing (2) and a pressure-sensitive adhesive layer (3) for attaching the

multilayer sheet to a smooth and rigid surface (5), wherein the pressure-sensitive adhesive is readily removable from the surface (5) and is selected to exhibit for an adhesive layer with a thickness of 300  $\mu\text{m}$  a 90° peel adhesion of between 20 and 85 N/inch from glass after a dwell time of 3 days at a temperature of 70°C. In a preferred 5 embodiment, the flexible backing (2) comprises at least one damagable layer (4) and shows intralayer failure when peeling off the multilayer sheet (1) from the surface (5).

The present invention furthermore refers to a pressure-sensitive adhesive which is obtainable by polymerizing a precursor comprising

- a) a monomer component which contains one or more alkyl acrylates, 10 the alkyl groups of which have an average of 4-14 C atoms and 2-8 phr of at least one copolymerizable monomer having a polar group,
- b) 5-15 phr of hydrophobic silica,
- c) one or more polymerization initiators, and
- d) one or more crosslinker compounds in a concentration resulting in a 15 crosslink density obtainable by using hexanedioldiacrylate as a reference crosslinker compound in a concentration between 0.06 and 0.14 phr.

The present invention furthermore refers to a pressure-sensitive adhesive which is obtainable by polymerizing a precursor comprising

- a) a monomer component which contains one or more alkyl acrylates, 20 the alkyl groups of which have an average of 4-14 C atoms, and more than 8-20 phr of at least one copolymerizable monomer having a polar group,
- b) 5-15 phr of hydrophobic silica,
- c) one or more polymerization initiators, and
- d) one or more crosslinker compounds in a concentration resulting in a 25 crosslink density obtainable by using hexanedioldiacrylate as a reference crosslinker compound in a concentration between 0.06 and 0.10 phr.

#### Detailed Description of the Invention

The multilayer sheet (1) of the present invention comprises a flexible 30 substrate (3) and a layer of pressure-sensitive adhesive (3) for attaching the film to a smooth and rigid surface (5) such as, for example, glass, metal or painted metal surfaces.

When trying to remove the multilayer sheet (1) from the surface, the flexible substrate (2) preferably shows intralayer failure thus imparting tamper-proof features to the multilayer sheet (1). The flexible substrate (2) can comprise one or more layers and preferably at least two layers. The flexible substrate (2) preferably comprises at least one damagable layer (4) which is designed to be the weakest point of the multilayer sheet (1) of the present invention and hence the predetermined failure point when peeling off the multilayer sheet (1) from the surface (5). The damagable layer (4) preferably is an inner, i.e., not exposed layer of the multilayer sheet (1) and has 2 adjacent layers of the multilayer sheet. The flexible substrate can comprises further layers such as, for example, a cover layer (6) (not shown), or a retroreflective layer (7).

The multilayer sheet (1) of the present invention can be readily removed from the surface (5) without any residue. The term "readily removable" means that the pressure-sensitive adhesive can be manually removed from the surface (5) after the period of use without using chemical agents such as organic solvents or mechanical tools such as knives or scrapers.

Due to the unique combination of tamper-proof features and ready removability from surfaces such as glass or painted metal, the multilayer films of the present invention comprising a damagable layer (4), are especially suited for the preparation of temporary labels such as toll vignettes on vehicles or anticounterfeiting labels on goods.

The pressure-sensitive adhesive useful for the multilayer sheet (1) of the present invention is selected to exhibit a high adhesion to the flexible substrate (2), i.e., to the layer of the flexible substrate (2) which is adjacent to the pressure-sensitive adhesive layer (3). In multilayer sheets according to the present invention comprising a damagable layer (4), this adhesion must be higher than the internal or cohesive strength of the damagable layer (4) in order to avoid that the flexible substrate can be clearly peeled from the adhesive layer without destroying the flexible substrate (2). The adhesion of the pressure-sensitive adhesive to the smooth and rigid surface (5) must also be higher than the internal strength of the damagable layer (4) in order to avoid that the multilayer sheet (1) is peeled off from the surface without destroying it. The adhesive must not only be resistant to easy peeling at ambient temperature, but must also adhere well and resist attempts to remove the multilayer sheet (1) intact at elevated

temperature. On the other hand, the adhesion between the pressure-sensitive adhesive layer and the smooth and rigid surface must not be so high as to result in permanent bonding of the pressure-sensitive adhesive layer to the surface (5).

It was found that pressure-sensitive adhesives which are useful in the multilayer sheets (1) of the present invention exhibit, for a layer of the pressure-sensitive adhesive in a thickness of 300 microns, a 90° peel adhesion from glass after a dwell time of 3 days at 70°C as measured by the test method specified below, of between 20 and 85 N/inch, and, especially, of between 30 and 75 N/inch, a very particularly of between 30 and 70 N/inch. The pressure-sensitive adhesive materials identified by this test method are useful for glass surfaces and other smooth and rigid surfaces, such as metal or painted metal surfaces. The pressure-sensitive adhesive materials are especially useful for glass surfaces.

The pressure-sensitive adhesive according to the present invention preferably exhibits a high optical transmission so that indicia (4d) such as printed patterns which form part of the flexible substrate (2), can be viewed through the adhesive layer (3). Pressure-sensitive adhesives exhibiting a transmission of visible light of at least 80% and preferably of at least 90% are preferred. The pressure-sensitive adhesives to be used in the multilayer films of the present invention are furthermore preferably optically clear, i.e., not colored.

It was found that a specific class of pressure-sensitive adhesives which fulfill the above requirements is obtainable by polymerizing a precursor comprising

- a) a monomer component which contains one or more alkyl acrylates, the alkyl groups of which have an average of 4-14 C atoms, and 2-8 phr of at least one copolymerizable monomer having a polar group,
- b) 5-15 phr of hydrophobic silica,
- c) one or more polymerization initiators,
- d) and one or more crosslinker compounds in a concentration resulting in a crosslink density obtainable by using hexanedioldiacrylate as a reference crosslinker compound in a concentration of between 0.06 and 0.14 phr.

These pressure-sensitive adhesives are new and they are subject matter of the present invention. Pressure-sensitive adhesive tapes containing hydrophobic silica are generally described in US 4,749, 590. The tapes are said to be initially repositionable,

5 "but within a few days they normally cannot be removed" (US 4,749,590, col. 4, lns. 49-50). US 4,895,745 describes dark acrylic pressure-sensitive adhesives comprising hydrophobic silica and pigments such as, for example, carbon black pigments which cannot be used, for example, for front face type stickers described below which require highly transmissive pressure-sensitive adhesives.

10 The term average of 4-14C atoms means that the average number of C atoms of the alkyl acrylate compounds, weighed by their respective percentage by weight with respect to the mass of the alkyl acrylate component, is between 4-14 and, in particular, between 4-12 C atoms.

15 Useful alkyl acrylates (i.e., acrylic acid alkyl ester monomers) include linear or branched monofunctional unsaturated acrylates or methacrylates of non-tertiary alkyl alcohols, the alkyl groups of which have from 4 to 14 and, in particular, from 4 to 12 carbon atoms. Examples of these lower alkyl acrylates used in the invention include but are not limited to, n-butyl acrylate, isobutyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, isoctyl acrylate, n-octyl acrylate, n-octyl methacrylate, 2-methylbutyl acrylate, isononyl acrylate, n-nonyl acrylate, isoamylacrylate, n-decyl acrylate, isodecyl acrylate, isodecyl methacrylate, isobornyl acrylate, 4-methyl-2-pentyl acrylate and dodecyl acrylate. Preferred lower acrylate and methacrylate esters include isoctyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isononyl acrylate and dodecyl acrylate.

20 The precursor preferably contains up to 5 and, in particular, 1-4 alkyl acrylates. The average number of carbon atoms in the alkyl groups of the alkyl acrylates as defined above, preferably is between 4-14, especially between 4-12 and very particularly between 5-10. The concentration of the alkyl acrylate component with respect to the mass of the precursor of the pressure-sensitive adhesive preferably is at least 75 wt.%, and, in particular, at least 85 wt.%.

25 The precursor of the PSA can contain alkyl esters of unsaturated aliphatic carboxylic acids other than acrylic acid such as, for example, alkyl maleates and alkyl fumarates (based, respectively, on maleic and fumaric acid). In this regard, dibutyl maleate, dioctyl maleate, dibutyl fumarate and dioctyl fumarate, are preferred. The amount of ester compounds of unsaturated aliphatic carboxylic acids other than acrylic acid preferably is not too high and, in particular, does not exceed 25 wt.% with respect to the mass of the alkyl acrylate component.

The term polar monomers includes both moderately polar and strongly polar monomers. Polarity (i.e., hydrogen-bonding ability) is frequently described by the use of terms such as 'strongly', 'moderately', and 'poorly'. References describing these and other solubility terms include 'Solvents', Paint Testing Manual, 3rd ed., G.G. Seward, Ed., American Society for Testing and Materials, Philadelphia, Pennsylvania, and 'A Three-Dimensional Approach to Solubility', Journal of Paint Technology, Vol. 38, No. 496, pp. 269-280. Examples for strongly polar copolymerizable monomers are acrylic acid, methacrylic acid and acrylamides while N-vinyl lactams such as, for example, N-vinyl pyrrolidone, N-vinyl caprolactam, acrylonitrile and dimethyl amino-propyl methacrylate are typical examples of moderately polar monomers.

The precursor contains between 2 and 8 phr of one or more copolymerizable polar monomers. If the amount of the copolymerizable polar monomers exceeds 8 phr, the 90° peel adhesion of the pressure-sensitive adhesive from glass is too high and the pressure-sensitive adhesive becomes permanently bonded. If the amount of the copolymerizable polar monomers is less than 2 phr, the 90° peel adhesion from glass is too low to ensure that the multilayer sheet (1) cannot be removed intact from a glass surface when applying for example, high temperatures.

The amount of the copolymerizable polar monomer preferably is from 2-7 phr and especially preferably from 3-6 phr.

The pressure-sensitive adhesive to be used in the multilayer films of the present invention furthermore comprises 5-15 phr of hydrophobic silica. In an especially preferred embodiment, the amount of the hydrophobic silica is between 7.5 and 15 phr and especially between 10 and 15 phr.

Hydrophobic silica is commercially available, for example, from Degussa, as "Aerosil" R972, R974 or R9976. According to a Degussa bulletin entitled "Product Information" of June 4, 1984, the hydrophobic silicas "Aerosil" R972, R974 and R976 are prepared from hydrophilic silicas denoted as "Aerosil" 130, 200 and 300, respectively, which exhibit a surface area of 130, 200 and 300 m<sup>2</sup>/g, respectively. Hydrophobic silica is furthermore commercially available, for example, as TS-720 from Cabot Cab-O-Sil Division, Tuscola, Illinois, USA. In US 2,859,198 (Sears et al.) it is proposed that the surface of finely-divided inorganic solid silicon-containing materials, such as silica, can be rendered hydrophobic by treating the material with an organo-

siloxane material. According to US 4,136,081 (Schultz), silica "can be treated with organosilicon materials such as chlorosilanes, silazanes, alkoxysilanes and cyclic siloxanes to produce hydrophobic surfaces" (col. 6, lns. 47-52).

5 The enumeration of hydrophobic silica materials given above, and the description of some selected methods for preparing hydrophobic silica materials is to be understood as illustrative and by no means limitative. The hydrophobic silica used to prepare the PSA materials according to the present invention, preferably exhibits a surface area of at least 10 m<sup>2</sup>/g and especially of at least 50 m<sup>2</sup>/g. The surface area of the hydrophobic silica especially preferably is between 50 to 400 m<sup>2</sup>/g (B.E.T. surface area).

10 The addition of hydrophobic silica to the precursor of the pressure-sensitive in the specified amount imparts a sufficient cohesive or internal strength to the pressure-sensitive adhesive so that the adhesive has a tough and rubbery character. This allows the adhesive residues to be removed, for example, from glass surfaces, by grasping the edge of the adhesive residue and pulling it to effect complete removal from 15 the glass substrate. Entire sections of adhesive residue or adhesive-coated sticker residue can then be removed manually. If the concentration of hydrophobic silica is chosen to be below 5 phr, the pressure-sensitive adhesive was found to break upon attempts to remove large sections of the adhesive mass, thus necessitating the use of mechanical tools and/or chemical agents such as organic solvents. Increasing the concentration of 20 the hydrophobic silica above 15 phr adversely affects the 90° peel adhesion properties from glass.

25 The addition of hydrophobic silica in a properly selected amount to the precursor of the pressure sensitive adhesives therefore is essential to establish the desired removability of the pressure-sensitive adhesive (3) from the surface (5). Other fillers such as, for example, hydrophilic silica or polysaccharide fillers were found to adversely affect optical properties such as clarity and/or mechanical properties such as 30 mechanical strength of the pressure-sensitive adhesive.

The precursor of the pressure-sensitive adhesive useful in the multilayer films of the present invention furthermore contains one or more crosslinker compounds to increase the cohesive strength and the tensile strength of the resulting PSA material.

Useful crosslinkers include benzaldehyde, acetaldehyde, anthraquinone, various benzophenone-type and vinyl-halomethyl-s-triazine type compounds such as, for

example, 2,4-bis(trichloromethyl)-6-p-methoxystyryl-s-triazine. Preferred are polyacrylic-functional monomers such as, for example, trimethylolpropane triacrylate, pentaerythritol tetraacrylate, 1,2-ethylene glycol diacrylate, tripropylene glycoldiacrylate, 1,6-hexanediol diacrylate or 1,12-dodecanediol diacrylate. The compounds listed above, which can be substituted or unsubstituted, are intended to be illustrative and by no means limitative.

The crosslinking component to be used in the present invention preferably contains 1-5, especially between 1-3 and very particular 1-2 crosslinker compounds. Especially preferred crosslinker compounds are 1,6-hexanedioldiacrylate and tripropylene glycoldiacrylate.

The degree of crosslinking (crosslink density) which can be expressed as the number of cross-links per gram or per unit volume of the polymer, can be estimated theoretically and determined experimentally, for example, by swelling measurements or via stress strain curves (see Encyclopedia of Polymer Science and Engineering, 2nd. ed., New York 1988, vol. 4, p. 355-357). A detailed description of swelling measurements which are preferred, is given in P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca and London, 1953, pg. 579. When reacting two different precursors which differ with respect to the crosslinker component but are otherwise identical, under identical external reaction conditions (polymerization method such as bulk, solution, emulsion or suspension polymerization, temperature, pressure, irradiation in case of UV-polymerization, etc.), the crosslink density obtained depends on the chemical nature of the crosslinkers used, their functionality and their respective concentrations. In the present application, the crosslink density is reported with respect to the crosslink density which is obtainable by using variable amounts of hexanediol diacrylate (HDDA) as a reference crosslinker component under standardized reaction conditions (bulk photopolymerization, photoinitiator: Irgacure 651, supplied by Ciba Geigy, in a concentration of 0.24 phr; UV irradiation with an exposure of 900-1500 mJ/cm<sup>2</sup> from an UV lamp, 90% of the emissions of which are between 300 and 400 nm, with a maximum at 351 nm; room temperature; normal pressure; exclusion of oxygen).

The precursor to be used in the multilayer sheets according to the present invention preferably contains one or more crosslinker compounds in a concentration to give a crosslink density obtainable by using HDDA in a concentration between 0.06 and

0.14 phr. The concentration of HDDA preferably is between 0.08 and 0.14 phr, and especially preferably between 0.09 and 0.13 phr.

If the crosslinker compounds are used in concentration to give a crosslink density obtainable by using HDDA in a concentration of less than 0.06 phr, the cohesive strength and the tensile strength of the resulting pressure-sensitive adhesive is too low. In this case, the adhesive layer was found to be cuttable, for example, with a razor blade, which allows intact removal of the multilayer film from the surface, without destruction, and permits readhesion of the multilayer sheet to another surface. If the crosslinker compounds are used in a concentration to give a crosslink density obtainable by using HDDA in a concentration of more than 0.14 phr, the 90° peel adhesion from the surface (5) was too low to ensure destruction of the flexible backing (2) comprising a damagable layer (4) when peeling off the multilayer film from the substrate.

The pressure-sensitive adhesive materials to be used in the multilayer sheets of the present invention can be obtained by applying generally known polymerization methods such as bulk, solution, emulsion or suspension polymerization. Due to environmental reasons bulk polymerization is often preferred in order to avoid using organic solvents.

The polymerization reaction is preferably started by means of a polymerization initiator and preferably proceeds via a radical polymerization mechanism. Useful examples of polymerization initiators include photoactivatable initiators such as, for example, benzoin ethers (e.g., benzoin methyl ether, benzoin isopropyl ether, substituted benzoin ethers such as anisoin methyl ether), acetophenones (e.g., 2,2-diethoxyacetophenone) or alpha-ketols (e.g., 2-methyl-2-hydroxy-propiophenone), and/or thermally activatable initiators such as, for example, organic peroxides (e.g., benzoyl peroxide and lauryl peroxide) and 2,2'-azobis(isobutyronitrile). Photopolymerization and the addition of photoactivatable initiators are preferred. The initiator component preferably comprises between 1-3 and, in particular, between 1-2 initiator compounds; especially preferred are initiator components containing only one photoinitiator. The initiator component is preferably present in an amount of 0.01-2.00 phr, in particular, between 0.05-1.00 phr and very specifically between 0.1-0.5 phr.

In a preferred method of preparation, a part of the initiator component is added to the alkyl acrylate component which is partly polymerized to a degree of

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typically 2-30% to form a syrup of coatable viscosity of, for example, 300-20,000 cps (Brookfield) at ordinary room temperatures. The viscosity of the syrup is preferably adjusted to the amount of hydrophobic silica to be added. For high loadings with hydrophobic silica of, for example, 12-15 phr, the viscosity of the syrup preferably is not more than 1,000 cps and, in particular, between 250 and 1,000 cps. For lower loadings with hydrophobic silica, the viscosity preferably is not less than 1,500 cps and, in particular, 1750 cps or more. The viscosity of the precursor can also be adjusted by adding a small amount of typically less than 5 phr of a polymeric additive which preferably is a photopolymerizable polyacrylate as is described, for example, in WO 94/00,052. The polymerization preferably proceeds as photopolymerization which is described, for example, in US 4,182,752. In a preferred embodiment, the polymerization is carried out with UV black lights having over 60 percent, and preferably over 75 percent of their emission spectra between 280 to 400 nm, with an intensity between about 0.1 to about 25 mW/cm<sup>2</sup>. The exposure is typically between 900-1,500 mJ/cm<sup>2</sup>. The polymerization may be stopped either by removal of the radiation or heat source and/or introduction of, for example, radical scavenging oxygen.

The filler component essentially comprising hydrophobic silica, is subsequently added to the prepolymerized syrup. When the amount of the hydrophobic silica exceeds about 8 phr, it has been found necessary to employ a high-shear mixer such as a paint mill to obtain uniform dispersions. By doing so and by properly adjusting the viscosity of the pre-polymerized syrup, essentially uniform dispersions can be obtained for loadings as high as about 25 phr. The pressure-sensitive adhesive used in the multilayer sheets of the present invention comprises up to 15 phr of hydrophobic silica.

The dispersion obtained is mixed with the remaining part of the initiator component and, optionally, with other adjuvants such as, for example, chain transfer agents, polymer additives like, for example, those described in EP 0,349,216 or EP 0,352,901, solvents, fire retardants, odor masking agents and/or other adjuvants known in the tape art. The addition of pigments and colorants is not preferred because the pressure-sensitive adhesives useful for the multilayer sheets of the present invention preferably exhibit a high optical transmission and clarity. If pigments/colorants and/or paints are added, these are preferably selected to impart color to the resulting PSA

materials without adversely affecting their transparency and clarity. An example of a suitable paint is Yellow Permalink CTL-Druckfarbe (printing paint) which is obtainable from SICPA Druckfarben, Backnang.

5 To produce PSA films useful in the multilayer sheets of the present invention, the above dispersion or mixture obtained is coated onto a backing, a carrier web or a release liner and polymerized in an inert, i.e. oxygen free atmosphere, for example a nitrogen atmosphere. Above and below, the term film is used to describe a structure whose thickness is substantially less than either its length or width and which has two, essentially parallel opposed surfaces. As used herein, the term films includes, 10 for example, sheets, ribbons, tapes and discs.

Damagable layers (4) for tamper-proof multilayer sheets (1) which are destroyed or irreversibly deformed when peeling off the multilayer sheet (1), have been described in the literature.

15 The incorporation of a damagable layer or damagable layers (4) into the multilayer sheets (1) of the present invention is optional but preferred. The present invention also comprises multilayer sheets comprising a flexible backing (2) and a pressure-sensitive adhesive layer (3) for attaching the multilayer sheet to a smooth and rigid surface (5) comprising no damagable layer (4).

20 The damagable layer (4) can comprise, for example, a pattern of adhesion-regulating material (4a) which can be applied onto the inner surface of the pressure-sensitive adhesive layer and/or of the other layers of the multilayer sheet (1) in a non-continuous fashion. The adhesion-regulating material covers only a part of the inner surface of one or more of these layers, thus creating surface areas with different adhesion properties. The adhesion-regulating material may be either an adhesion-reducing substance such as a release agent or, alternatively, an adhesion-promoting 25 substance such as a primer.

30 An adhesion-reducing pattern (4a) may be applied, for example, onto the inner surface of the pressure-sensitive adhesive layer (3). While the adhesion of the pressure-sensitive adhesive layer (3) to the adjacent layer of the flexible substrate is high in areas where the adhesion-reducing material is absent, adhesion between the pressure-sensitive adhesive (3) and the adhesion reducing material is very low in areas where the adhesion-reducing material is present. In area where the adhesion-reducing material is

present, there is often practically no adhesion between the pressure-sensitive adhesive layer (3) and the adjacent layer of the flexible substrate.

Several materials can be used as adhesion-reducing or adhesive-repellent substances in order to create a pattern (4a). Examples of these materials include carbamates like polyvinyl octadecyl carbamate, available under the name "Kalle release coat K" from Hoechst AG, Germany, or "Escoat P20" from Aderson Development Company, USA. Further suitable materials include silicone systems like UV-curable free-radical silicone acrylate release coatings, silicone addition systems, silicone condensation systems and cationically-curing silicone systems.

A more complete description of both the silicone and non-silicone based adhesion-reducing materials and their use to create patterns can be found, for example, in US 5,061,535.

The adhesion-regulating material used in the multilayer sheets (1) of the present invention may also be an adhesion-promoting substance. Layers on either side of the pattern of an adhesion-promoting substance exhibit increased adhesion in areas where the adhesion-promoting substance is present. In areas where the adhesion-promoting substance is absent, there is limited adhesion or occasionally even no adhesion between the adjacent layers.

Several types of materials are useful as adhesion-promoting substances. These must be tailored specifically to the two adjacent layers, in that the adhesion-promoting substance must have good adhesion to both adjacent layers which may be widely different in chemical nature. Both polyurethane based primers and ethylene-acrylic acid based primers have been found suitable for use in the present invention.

The type of pattern used for application of the adhesion-regulating substance in the present invention is not critical.

The adhesion-regulating pattern (4a) is preferably an adhesion-promoting substance and is preferably applied using a gravure printing method.

The adhesion-regulating pattern (4a) provides areas with different adhesion properties for the adjacent layers of the flexible backing (2) resulting in deformation and/or destruction of the adjacent layer or layers. In this sense, the adhesion-regulating pattern (4a) is termed as a damagable layer in the multilayer sheets of the present invention.

The damagable layer (4) can also comprise certain frangible optical elements or layers such as a kinegram (4b) or a hologram (4b) as is described, for example, in EP 0,253,089; EP 0,401,466 and US 5,066,041. During an attempt at tampering, the hologram would be destroyed. Kinegrams which are commercially available from Landis & Gyr, Zug, Switzerland, and others, and holograms are very attractive from an aesthetic point of view and they can be used to incorporate user-specific graphics or information into the films. Kinegrams or holograms can be used in restricted areas of the multilayer film only, but it is also possible to use extended holographic layers which comprises a structured layer and an optional reflective layer.

The structured layer can be formed by several methods that are well known in the art, disclosed in US 4,856,857. It may be made of materials such as polymethyl methacrylate, nitrocellulose, and polystyrene. The structured layer includes a microstructured relief pattern of holographic or diffraction grating images in the form of logos or patterns that reflect light. In one embodiment, an embossed microstructured layer may be formed by contacting the material from which the structured layer will be made with a non-deformable embossing plate having a microstructured relief pattern, and applying heat and pressure. Alternatively, the structured layer may be made by any other suitable process, such as radiation curing, and may be made of materials such as urethane, epoxy, polyester, and acrylate monomers and oligomers, which are formulated with photoinitiators, cast on a non-deformable tool having a microstructured relief pattern, and radiation cured.

The optional reflective layer is coated on the structured layer of the holographic layer (4b) either before or after embossing. The reflective layer preferably has a higher refractive index than the structured layer. In a preferred embodiment, the reflective layer is substantially transparent and colorless. Illustrative examples of suitable reflective layer materials include but are not limited to bismuth trioxide, zinc sulfide, titanium dioxide, and zirconium oxide, which are described in US 4,856,857. Less transparent materials such as thin aluminum or silver, or patterned reflectors can also be used. The reflective layer enhances the reflection of light through the structured layer due to the difference in refractive index between the structured and reflective layers. Thus, the structured holographic pattern is more readily visible to the unaided eye once the reflective layer is coated on the structured layer, and the pressure-sensitive adhesive

can be directly applied to the structured layer without diminishing the visibility of the structured pattern.

The transparent multilayer film described in DE 44 24 148.8 comprises a 5 destructible or irreversibly deformable layer (4c) comprising, for example, a hot-melt adhesive or a pressure-sensitive adhesive, which also can be used in the multilayer sheets (1) of the present invention. The destructible or irreversibly damagable layer (4c) may also comprise, for example a paper layer whereby the internal strength and the thickness of the paper layer are selected in a manner so that the paper layer is a predetermined breaking point of the multilayer sheet (1).

10 The damagable layer can also comprise indicia (4d) which can be applied by any number of processes, including transfer processes or direct printing processes. Indicia are preferably applied by standard printing processes, such as screen printing. Screen printing inks commonly used for this purpose include 3M screen-printing inks (800 series, 900 series), dried in a forced air oven at 45°C. for 30 min. (800 series) or 15 for 45 sec. at 65°C. (900 series). Inks should preferably be selected which can be dried or cured at relatively low temperatures for short periods of time, to facilitate rapid manufacturing and prevent damage of thermally sensitive layers which may be present. Printed patterns and other indicia may operate as damagable layers only when used as an inner layer having two adjacent layers of the multilayer sheet. Top-printings, for 20 example, usually do not operate as damagable layers.

The use of printed patterns as a damagable layer is described, for example in US 4,121,003 and US 4,184,701.

The specific embodiments of the damagable layer described above are intended to be illustrative and not limiting.

25 The term "damagable layer" is used in the present invention to characterize readily damagable, i.e. destructible and/or inelastically deformable layers which can be continuous or discontinuous. The damagable layer exhibits a low internal or cohesive strength and is the predetermined breaking point of the multilayer sheet upon removing or attempts at tampering. It should be noted, however, that a multitude 30 of failure patterns is observed for the multilayer sheet of the present invention in practice. The failure process is relatively complex and is influenced by various parameters such as the elasticity or brittleness, respectively, of the different layers, the

tensile strength of the materials used and the adhesion between the adjacent layers, the thickness of the different layers, the respective pattern of discontinuous layers if present, the peel direction and peel angle, the peel strength and peel speed and the temperature during peeling. The failure pattern may change when varying one or more of the 5 parameters. On tampering, the internal strength of damagable layers of type (4c), for example, may increase in some cases as a result of stretching and simultaneous orientation of macromolecules in the damagable layer so that one or more other areas of the multilayer sheet have similar or even less internal strength and/or adhesion with respect to adjacent layer or layers than the damagable layer. This means in practice a 10 layer or layers of the multilayer sheet other than the damagable layer may be deformed and/or irreversibly destructed prior to the damagable layer and/or in addition and/or instead of the damagable layer. multilayer sheets (1) with one or more damagable layers (4) are subject-matter of the present invention irrespective of the actual failure mode, i.e. irrespective of whether the failure pattern relies on damaging of the damagable layer or 15 layers and/or of other layers.

The multilayer sheet (1) can furthermore comprise a cover layer (6) (not shown) which forms the exposed layer opposite to the adhesive layer.

The cover layer (6) (not shown) of the multilayer sheet according to the 20 invention is typically a polymeric film which is preferably dimensionally stable, wear-resistant, tear resistant, abrasion resistant and/or solvent resistant. The cover layer may be corona-treated, flame-treated, plasma-treated or treated with a chemical primer.

Methods for the treatment of surfaces are described, for example, in G. Habenicht et al., Adhesion, 1992(5), pp. 21-36 and in K.W. Gerstenberg, Coating, 1990, pp. 260-263.

25 A material which is preferred for this purpose is, for example, a polyethylene terephthalate (PET) polymeric film. The dimensionally stable, wear-resistant, tear resistant, abrasion resistant and/or solvent resistant cover layer protects the underlying layers of the multilayer sheet (1) from wear, dirt, moisture and other undesirable influences during its lifetime.

30 The cover layer preferably has a thickness of from 10 to 200 microns and more preferably from 10 to 150 microns. Especially preferred is a thickness from about 10 to about 75 microns. In order to improve adhesion to the underlying layer, the film is

preferably treated with corona discharge or with a chemical primer. The primer can be applied in the customary manner, for example with a coating rod, at a useful thickness of up to about 1 micron.

The multilayer sheet (1) according to the invention can furthermore comprise a reflective layer (7) which enhances its visibility. Incorporation of a reflective layer (7) is optional but preferred. The reflective layer can be a metal layer such as a thin metal foil, for example, or it can comprise one or more types of retroreflective materials, including microsphere-type retroreflective materials and cube corner-type retroreflective materials. The retroreflective layer disclosed in US 2,407,680 may comprise an enclosed monolayer of glass microspheres which are coated in a spacing resin comprising, for example, polyvinyl butyral or polyester. The spacing resin conforms to the microspheres. A reflector layer which underlies the spacing resin may comprise opaque materials such as silver, aluminum, chromium, nickel, or magnesium, or transparent high-index reflector materials such as those described above for use on the holographic structured layer, such as zinc sulfide, or multilayer reflectors as described in US 3,700,305. Thus, light that enters the retroreflective layer is focused by the glass microspheres through the spacing resin, and reflected by the reflector layer back through the spacing resin and glass microspheres to an observer. Other retroreflective materials using glass microspheres are described in US 3,801,183. Microsphere-type retroreflective materials are commercially available, for example, from 3M, St. Paul, USA, as 3M® SCOTCHLITE® High Intensity Vehicle Marking Sheeting Series No. 790; 3M® SCOTCHLITE® Validation Security Sheeting Series No. 5300, 5350, 5390, 4250, and 4290; 3M® SCOTCHLITE® Label Sheeting Series No. 5330; and 3M® SCOTCHLITE® Face Adhesive Verification Sheeting Series No. 2500.

The retroreflective layer (7) may also include a multiplicity of cube-corner retroreflective elements, instead of glass microspheres and resin, that may be made of materials such as vinyl, polycarbonate, or acrylic polymers for embossed cube-corner retroreflective elements, and urethane, epoxy, polyester and acrylate oligomers and monomers for radiation-cured cube-corner retroreflective elements. The cube-corner elements typically have three mutually perpendicular faces with surface areas of between approximately  $1.9 \times 10^{-3}$  mm<sup>2</sup> to 0.1 mm<sup>2</sup>. Cube-corner retroreflective elements can be embossed by a master mold into a sheeting material under suitable

temperature and pressure. The elements may also be created by coating a radiation-curable resin onto a master mold, laminating an overlay film under sufficient pressure, and solidifying the resin by curing it with radiation.

5 The thickness of each of the various layers forming the flexible substrate (2) are preferably selected to be within the range of 10 to 1000 microns, preferably 15-500 microns, and most preferably 20-200 microns.

10 The materials forming the layers of the multilayer sheet (1) of the invention can be brought together and bonded to one another using a variety of known coating and lamination processes. Typically the pressure-sensitive adhesive layer (3) is laminated to the flexible substrate (2) by a transfer process using only pressure. Layers of the flexible substrate (2) are commonly combined using lamination equipment at either ambient or elevated temperatures.

15 In cases of non-continuous layers such as patterns forming indicia or patterns forming layers of adhesion regulating substances, these patterns may be applied by standard printing techniques such as gravure printing or screen printing. Non-continuous layers may also be formed separately on a temporary substrate such as a release liner, for example and transferred onto other component layers of the multilayer film by lamination as well.

20 Figure 1 shows a multilayer sheet (1) according to the present invention, comprising a pressure-sensitive adhesive layer (3) which is adhered to a destructible or irreversibly deformable layer (4c) which has an indicia layer (4d) on its inner surface. The destructible or irreversibly deformable layer (4c) can be, for example, a paper layer. Upon attempts to remove the multilayer film from the substrate, the indicia layer (4d) breaks, followed or accompanied by an irreversible deformation and/or destruction of 25 the layer (4c) and/or the adhesive layer (3).

When using a paper layer as the destructible or irreversibly deformable layer (4c), the type of paper and the thickness of the paper should be selected so that the paper layer splits and is irreversibly damaged upon tampering.

30 If the destructible or irreversibly deformable layer (4c) is an opaque layer like, for example, a paper layer, the multilayer sheet of Fig. 1a can be applied, for example, onto a glass surface or on the surface of another transparent, smooth and rigid material, like for example, polymethylmethacrylate sheeting and viewed from the

opposite side of the transparent material through the transparent adhesive. This construction, which will be termed above and below as a front face type construction, can be used, for example, for a windshield sticker which is applied to the windshield from the inside of the vehicle and viewed from the outside.

5        Fig. 1b shows a multilayer film similar to that of Fig. 1a whereby the sequence of layer (4c) and indicia layer (4d) have been reversed. This construction which will be termed above and below as rear face type construction, can be used, for example as a tamperproof and removable label or sticker which is adhered via a pressure-sensitive adhesive layer (3) to a non-transparent surface such as a painted metal surface. In this case the viewer looks at the printed pattern or indicia layer (4d). In this construction the printed pattern or indicia layer (4d) does not form a predetermined breaking point, because this layer is applied on top of layer (4c) and does not form an inner layer as in case of Fig. 1a.

10      In another embodiment which is derived from the embodiments shown in Fig. 1a and 1b but is not shown, the destructible or irreversibly deformable layer (4c) is replaced with a retroreflective layer (7), and the tamper-proof properties are primarily based on the indicia layer (4d).

15      Figs. 2a shows a multilayer sheet (1) according to the present invention comprising a pressure-sensitive adhesive layer (3) bearing an indicia layer (4d). The adhesive layer bonds to a transparent or semitransparent holographic layer (4b) such as a microstructured holographic layer. The transparent holographic layer is bonded to the light-entrant surface of a retroreflective layer (7) using a pattern-coating of an adhesion-promoting substance (4a) such as a primer. The pattern coating of primer promotes adhesion of the thin, frangible holographic layer in areas where it is present, thus causing the irreversible destruction of the holographic layer (4b), and any indicia (4d) it might bear, upon attempts at tampering.

20      The embodiment of Fig. 2a is a front face type construction which is viewed through the pressure-sensitive adhesive layer and the transparent material it is adhered to.

25      Fig. 2b is a rear face type construction which corresponds to the construction of Fig. 2a. In this construction the printed pattern or indicia (4d) does not

form a predetermined breaking point because this layer is applied on top of layer (4b) and does not form an inner layer as in case of Fig. 2a.

The failure modes described for the embodiment of Fig. 1 and 2 are illustrative and not limiting, and further failure patterns which are, for example, 5 intermediate between the failure modes described are observed in practice.

It was furthermore found by the present inventors that a pressure-sensitive adhesive which is obtainable by polymerizing a precursor comprising

- a) a monomer component which contains one or more alkyl acrylates, the alkyl groups of which have an average of 4-14 C atoms, and more than 8-20 phr of 10 at least one copolymerizable monomer having a polar group,
- b) 5-15 phr of hydrophobic silica,
- c) one or more polymerization initiators, and
- d) one or more crosslinker compounds in a concentration resulting in a crosslink density obtainable by using hexanedioldiacrylate (HDDA) as a reference 15 crosslinker compound in a concentration between 0.06 and 0.11 phr,

exhibits advantageous 90° peel adhesion values on smooth and rigid surfaces such as glass or painted metal surfaces, and these pressure-sensitive adhesive materials are subject-matter of the present invention. The concentration of the reference crosslinker HDDA preferably is from 0.06-0.10 and especially preferably from 0.06- 20 0.09.

While the pressure-sensitive adhesive material described above which is useful for the preparation of the pressure-sensitive adhesive layer (3) of multilayer sheet (1) comprises an amount of the copolymerizable monomer or monomers of between 2-8 phr, it was found that useful pressure-sensitive adhesive materials with high values of 25 90° peel adhesion from glass are obtained when varying the amount of the copolymerizable monomers having a polar group from more than 8-20 phr, preferably from more than 8-15 phr and especially preferably from more than 8-10 phr. The pressure-sensitive adhesives are new and subject-matter of the present invention. In these pressure-sensitive adhesive materials the alkyl acrylates, the copolymerizable 30 monomers having a polar group, the polymerization initiators and the crosslinker compounds can be selected as is described above for the pressure-sensitive adhesive

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useful for the pressure-sensitive adhesive layer (3), and these materials can be prepared as indicated above.

The multilayer sheets (1) of the present invention are readily removable from rigid surfaces such as glass or painted metal and they are especially useful for the preparation of temporary labels and stickers such as toll vignettes which are to be removed after a specific period of use. In a preferred embodiment the multilayer sheets (1) comprise one or more damagable layers (4) and exhibit a unique combination of tamper-proof features, and complete and ready removability.

The present invention is further explained by the following examples which are illustrative, but not limitative. The following test methods are used to characterize the materials used in the examples.

#### Test Methods

##### 90° peel adhesion from glass

The 90° peel adhesion test is a modified version of PSTC-3 which is available from the Pressure Sensitive Tape Council of Glenview, Illinois, USA. A flexible retroreflective sheeting (3M® Scotchlite® 4780A without EAA top film, available from 3M, St. Paul, USA) was substituted for the polymeric film normally used as a backing in this test.

The adhesive layer to be tested was produced by photopolymerizing the prepolymerized precursor between two layers of siliconized biaxially oriented polyethylene terephthalate (PET) film having a thickness of 50 microns. Strips of the adhesive material between the two polyester sheets were cut into widths of 2.54 cm and lengths of 11 cm for us in this test.

One of the polyester sheets was removed and the exposed adhesive face laminated to the retroreflective side of a commercially available retroreflective sheeting (see above) with a rubber-coated roller. The roller was passed over the sample 5 times with a pressure that can be exerted by hand. The adhesive/reflective sheeting laminate thus prepared was then stored at 23° C for 24 hours.

The second polyester sheet was then removed and the exposed adhesive face applied to a glass plate (side not exposed to metal bath during production) which

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had been cleaned with isopropyl alcohol. The adhesive/retroreflective sheeting laminate was pressed onto the glass surface using a conventional mechanical laminator. The lamination was performed with a rubber-coated roller weighing 6.8 kg which was passed over the sample 4 times at a rate of 300 mm/min.

5 Samples were then stored at various conditions before the peel adhesion measurements were made. Peel adhesion at 90° peel angle were then made at 23°C with a peel rate of 300 mm/min. using a tensile tester.

10 Three measurements were made for each sample. The values were then averaged and recorded in N/in (N/2.54 cm).

10

#### Removability Test

15 Pressure-sensitive adhesive compositions were photopolymerized between two siliconized transparent polyester sheets. One polyester film was removed from the adhesive layer thus formed and the exposed adhesive surface applied to a multilayer backing (2). The two materials were laminated together using a rubber-coated roller. The roller was passed over the sample 5 times with a pressure that can be exerted by hand. The adhesive/reflective sheeting laminate thus prepared was then stored at 23°C for 24 hours.

20 The remaining polyester sheet protecting the pressure-sensitive adhesive layer was then removed. The final multilayer sheet (1) was then adhered to a glass substrate using a conventional mechanical laminator. The lamination was performed with a rubber-coated roller weighing 6.8 kg which was passed over the sample 4 times at a rate of 300 mm/min.

25 The behavior of the multilayer sheet (1) was evaluated qualitatively during attempts to peel the multilayer sheet from glass by hand.

#### Examples 1-5 and Comparative Examples 1-5

30 A mixture of 0.04 phr of Irgacure 651 (commercially available through Ciba-Geigy) and 100 parts by weight of iso-octylacrylate (IOA) was partially polymerized by UV light to form a syrup of a coatable viscosity of about 2,000 mPas. Then as indicated in Table 1 various amounts of hydrophobic silica, hexanediol diacrylate (HDDA) and, in each case, 0.2 phr of Irgacure 651 (commercially available

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through Ciba-Geigy) were added to the syrup followed by mixing with a lab stirrer for 90 minutes. The coating and curing of the syrup were performed between two transparent siliconized polyester films. The level of radiation dosage was about 1,300 mJ/cm<sup>2</sup>. The radiation was supplied from lamps having about 90% of the emissions between 300 and 400 nm, and a peak emission at 351 nm. The thickness of the adhesive samples was chosen to be 300 or 800 µm.

Table 1 Adhesive compositions used in the examples

Adhesive	Isooctyl acrylate	Acrylic acid	Hydrophobic silica (1)	HDDA (2)
A	96.5	3.5	15	0.13
B	95	5	10	0.12
C	96.5	3.5	10	0.12
D	98	2	10	0.12
E	92	8	10	0.12
cA	100	0	15	0.3
cB	90	10	15	0.12
cC	90	10	12.5	0.12
cD	90	10	10	0.12

(1) Hydrophobic fumed silica, available as R-972 from Degussa.

(2) HDDA = hexanedioldiacrylate

#### Examples 1-5

90° peel adhesion was measured for the adhesives of Examples 1-5 and comparative Examples 1-5 as described above. It is evident that high adhesion values were present initially for the adhesives of Examples 1-5 and were maintained after aging and adhesive bond under various conditions. The adhesive bond could still be broken if sufficient force was applied and the adhesive could be removed completely.

Contrary to this pressure-sensitive adhesive compositions of Comparative Examples 1-5 exhibit adhesion to glass which is either too high (C2-C5) or too low (C1) to be useful for the particular application envisioned.

Table 2 Results of peel adhesion tests

Ex.	Adhesive comp.	Adhesive thickness (microns)	Glass, 20 min, 23°C. (N/in.) peel at 23°C	Glass, 3 days, 23°C. (N/in.), pecl at 23°C	Glass, 3 days, 70°C. (N/in.), pecl at 23°C	Painted metal, 20 min, -10°C°, (N/in.), pecl at -10C°
1	A	800	76.0.	60.0	74.9	--
2	B	300	73.2	36.8	52.8	--
3	C	300	32.8	33.0	41.5	27.2
4	D	300	29.2	30.1	33.4	14.0
5	E	300	38.9	49.6	80.9	--
C1	cA	800	10.6	9.4	9.4	--
C2	cB	800	28.6	57.1	*	--
C3	cC	800	47.1	64.9	*	--
C4	cD	800	62.9	73.0	*	--
C5	cD	300	57.9	63.4	*	--

\* construction break, adhesion too high to be measured, adhesive not completely removable without solvents and/or mechanical tools

5

### Examples 6-8 and Comparative Example 6

The pressure-sensitive adhesive materials shown in Table 3 were obtained by using the method of Examples 1-5.

10

Table 3

Adhesive	IOA	AA	Hydrophobic silica	HDDA
F	90	10	15	0.06
G	90	10	15	0.08
H	90	10	15	0.10
cE	90	10	15	0.12

90° peel adhesion was measured for the adhesives of Examples 6-8 and Comparative Example 6 using the test method specified above. The results are summarized in Table 4.

15

Table 4

Example	Adhesive comp.	Adh. thickness, microns	Glass, 3 days, 23°C, (N/1.27 cm)
6	F	800	73.2
7	G	800	77.9
8	H	800	65.3
c6	cE	800	47.1

## Example 9

5 A multilayer backing (2) was prepared by the following procedure:

1. A polyester film (= backing) was heat laminated onto the aluminum side of a retroreflective sheeting based on microspheres. The laminate backing/retroreflective sheeting is available from 3M, St. Paul, USA as 3M® Scotchlite® FAVS sheeting 2005 E.
- 10 2. A pattern of ethylene-acrylic acid based adhesion-promoting primer 70:30 wt.% mixture of Neocryl A45 (commercially available from Zenica, Netherlands) and Adcoate 50 T 4990 (commercially available from Morton, USA) was then applied to the front or face side of the retroreflective sheeting used above by a simplified hand printing process to generate a regular array of spots of approximately 3 cm in diameter.
- 15 3. A sheet of the material thus prepared was cut into samples of approximately 6 cm x 4 cm.
- 20 3. A thin transparent film bearing a hologram was then heat laminated to the front surface of the reflective sheeting bearing the patterned adhesion-promoting substance. The holographic film which is commercially available from Crown Roll Leaf, Inc. of Peterson, New Jersey, was a thin transparent hologram transfer film, which consisted of a polyester liner, a polymethyl methacrylate based structured layer, a high-index zinc sulfide reflector, and a thin adhesive. Lamination was performed at approximately 130°C. with a pressure of 2 bar and a speed of 5 cm per minute using a commercially available heat laminator (Sallmetal, Raalte, The Netherlands).

4. An image was then screen-printed on top of the transparent holographic layer using a commercially available screen-printing ink (3M screen-printing ink 882 (red)). The ink was dried 30 min. at 45°C.

5 A 300 micron thick layer of pressure-sensitive adhesive of Example 2 was applied by first removing one of the protective liners and then laminating the PSA to the screen-printed surface using a rubber-coated roller passed over the sample 5 times using that pressure which could be exerted by hand, thus preparing a front face type multilayer sheet (1) of the invention.

10 Effectiveness of the complete adhesive-coated multilayer sheet construction was evaluated by first removing the second protective liner, adhering the multilayer sheet to a glass test surface and qualitatively evaluating the removal behavior as described under the "Removability test" method above. After multilayer sheet removal, several areas were examined for the presence of residues: 1) the glass substrate; 2) areas of the retroreflective layer where adhesion-promoting substance had 15 been applied; and 3) areas of the retroreflective layer where no adhesion-promoting substance was applied. Results of the removability test are given in Tables 6 and 7.

#### Example 10

20 Example 10 was prepared in an identical manner to Example 9, with the exception that the pressure-sensitive layer of Example 3 was applied to the face of the multilayer sheet at a thickness of 300 microns. Results of the removability test are given in Tables 6 and 7.

#### Example 11

25 Example 11 was prepared in an identical manner to Example 9, with the exception that a 300 micron layer of the PSA of Example 4 was applied to the face of the multilayer sheet. Results of the removability test are given in Tables 6 and 7.

#### Example 12

30 Example 12 was prepared in an identical manner to Example 9, with the exception that a different screen-printing ink was employed. The screen-printing ink applied to the pattern-coating of primer on the retroreflective layer was 3M screen-

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printing ink 910 (blue), dried 45 sec. at 65°C. Results of the removability test are given in Tables 6 and 7.

#### Example 13

5 Example 13 employed a multilayer sheet as described in Example 12, with the exception that the polyester film present on the aluminum-coated side of the retroreflective sheeting was omitted. As in Example 12, a 300 micron layer of the pressure-sensitive adhesive denoted B was present. The adhesive layer was laminated to the aluminum-coated side or rear side of the retroreflective sheeting, however, rather  
10 than the front face, thus creating a rear face type multilayer sheet suitable for application to a painted metal surface such as a motorcycle body.

#### Examples 14-15

15 Examples 14 and 15 were prepared in the same manner as Example 13, with the exception that the pressure-sensitive adhesives denoted as C and D, respectively were employed at a thickness of 300 microns.

Table 5 Construction of Examples 9-15

(The order in the Table reflects the construction of the multilayer sheet.)

Ex.	PSA, microns	backing	retrorefl. sheeting	primer	hologram	print	PSA, microns
9		x	x	x	x	ink 1	B, 300
10		x	x	x	x	ink 1	C, 300
11		x	x	x	x	ink 1	D, 300
12		x	x	x	x	ink 2	B, 300
13	B, .300	*)	x	x	x	ink 2	
14	C, 300	*)	x	x	x	ink 2	
15	D, 300	*)	x	x	x	ink 2	

Ink 1 3M screen-printing ink 882 (red), dried 30 min. at 45°C

5 Ink 2 3M screen-printing ink 910 (blue), dried 45 sec. at 65°C

\*) 3M® Scotchlite® FAVS sheeting 2005 E without polyester backing

Table 6 Results of removability tests (1 hr. 23°C)

Example	Residue on glass	Residue on primed area	Residue on unprimed area
9	Adhesive, portions of hologram and ink	Hologram and ink	No residue
10	Adhesive, portions of hologram and ink	Hologram and ink	No residue
11	Adhesive, portions of hologram and ink	Hologram and ink	No residue
12	Adhesive, portions of hologram and ink	Hologram and ink	No residue

Adhered multilayer sheets of Examples 9-15 were stored under a variety of conditions as indicated in the Table and then removed from glass. All failures indicated that the tamper-proof features of the multilayer sheets such as layer splitting

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were operational. Adhesive residues and/or backing residues on the glass substrate were all completely removable by hand.

Sticker temp., °C	Glass temp., °C	Storage conditions, time and temp, °C.	Removal conditions, approx. temp, °C.
23	23	1 hour, 23°	23°
23	-30	2 days, -30°	-30°
23	-30	2 days, 40° (90%r.h.)	40°
23	-30	1 wk, -30°	-30°
-6	11	2 days, 23°	23°
-6	11	2 days, -30°	-30°
-6	11	1 wk, -30°	-30°
-6	11	2 days, 40°(90%)	40°
-6	11	1 wk, 23°	23°

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6. Multilayer sheet (1) according to any of claims 2-5 with a sequence of layers (3)/(4d)/(4a)/(7), (3)/(7)/(4a)/(4d), (3)/(4d)/(4b)/(4a)/(7) or (6)/(4d)/(4b)/(4a)/(7)/(3).

5

7. Use of the multilayer sheet (1) according to any of claims 1-6 for preparing temporary labels or stickers such as toll vignettes.

8. Pressure-sensitive adhesive which is obtainable by polymerizing a precursor comprising

a) a monomer component which contains one or more alkyl acrylates, the alkyl groups of which have an average of 4-14 C atoms, and 2-8 phr of at least one copolymerizable monomer having a polar group,

b) 5-15 phr of hydrophobic silica,

c) one or more polymerization initiators, and

d) one or more crosslinker compounds in a concentration resulting in a crosslink density obtainable by using hexanedioldiacrylate as a reference crosslinker compound in a concentration between 0.06 and 0.14 phr.

9. Pressure-sensitive adhesive which is obtainable by polymerizing a precursor comprising

a) a monomer component which contains one or more alkyl acrylates, the alkyl groups of which have an average of 4-14 C atoms, and more than 8-20 phr of at least one copolymerizable monomer having a polar group,

b) 5-15 phr of hydrophobic silica,

c) one or more polymerization initiators, and

d) one or more crosslinker compounds in a concentration resulting in a crosslink density obtainable by using hexanedioldiacrylate as a reference crosslinker compound in a concentration between 0.06 and 0.11 phr.

1/1

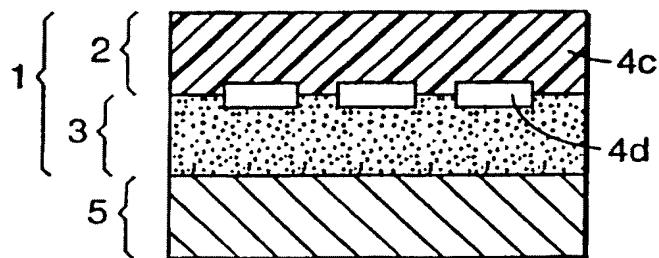


Fig. 1a

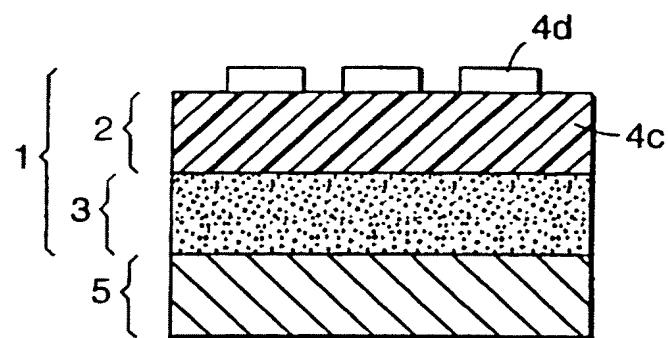


Fig. 1b

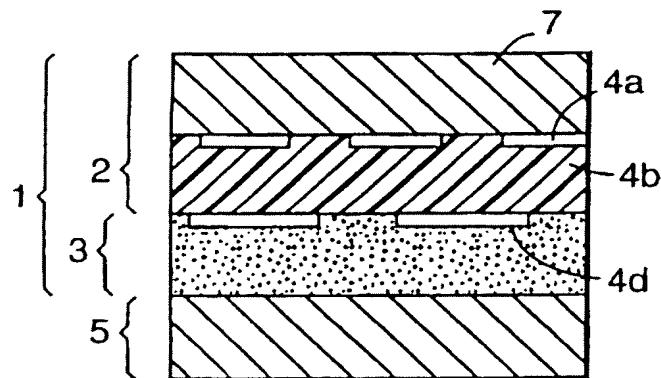


Fig. 2a

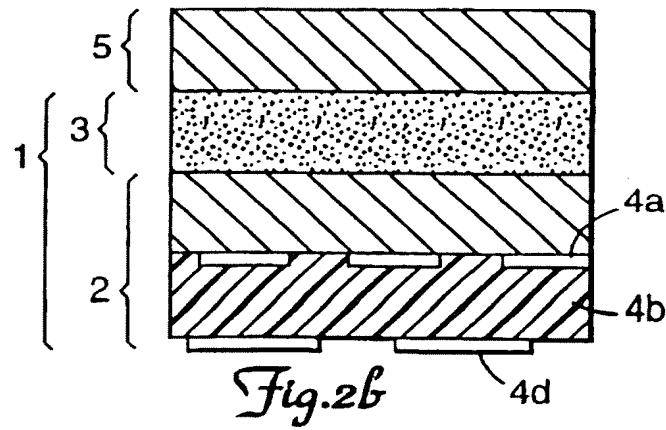


Fig. 2b

# INTERNATIONAL SEARCH REPORT

Intern	Application No
PCT/US 97/08528	

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 G09F1/00 B32B7/12 G09F3/02 C09J7/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B32B G09F C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 585 076 A (P P PAYNE LTD) 2 March 1994 see claims ---	1-9
A	EP 0 651 365 A (MINNESOTA MINING & MFG) 3 May 1995 see figures 2,3 see claims ---	1-9
A	US 5 202 361 A (ZIMMERMAN PATRICK G ET AL) 13 April 1993 see claims -----	3,8,9

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

2 September 1997

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

Interr	Application No
	PCT/US 97/08528

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